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Rheological Molecular Weight Distribution Determinations of Ethylene/Tetrafluoroethylene Copolymers: Implications for Long-Chain Branching

William H. Tuminello*

E. I. du Pont de Nemours & Company, Inc., Experimental Station, P.O. Box 80356, Wilmington, Delaware 19880-0356

Warren H. Buck

E. I. du Pont de Nemours & Company, Inc., Experimental Station, P.O. Box 80353, Wilmington, Delaware 19880-0353

Dewey L. Kerbow

E. I. du Pont de Nemours & Company, Inc., Washington Works R&D, P.O. Box 1217, Parkersburg, West Virginia 26102

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ABSTRACT: The molecular weight distributions of ethylene/tetrafluoroethylene copolymers (PETFE) were estimated by dynamic mechanical analysis of their melts. The validity of the method had been established on model polystyrenes. The high temperatures required for solubility prevented analysis by classical techniques. Our results indicated much broader distributions than determined by Chu and co-workers[1-3] on dilute PETFE solutions using a unique high-temperature laser light scattering procedure. Dynamic mechanical analysis was performed on one of the samples after dissolution, filtering, and drying to reveal no significant change versus the originally analyzed melt. This indicated that the conditions required to treat the solutions during the light scattering tests were not appreciably altering the polymer nor filtering out an insoluble portion. A broader distribution would be predicted by the rheological technique if long-chain branching were present. Strong evidence for the presence of such branching was observed when plotting the zero shear viscosity (from the rheological analysis) versus the weight-average molecular weight (from light scattering). The well-known 3.4 power law would have been obtained if these were linear chains. Instead, we observed a much stronger effect of molecular weight on viscosity which has been attributed to the effects of long-chain branching. The theory of portions of the PETFE chain acting as its own chain-transfer agent is a potential explanation for branch formation.

Introduction

Alternating ethylene/tetrafluoroethylene copolymers (PETFE) with nearly equal molar ratios of the comonomers are high melting polymers which form stable solutions only at temperatures above 200 °C. Therefore, classical techniques of molecular characterization (like size-exclusion chromatography) have generally not been used because they require dilute solutions at temperatures less than about 150 °C. Despite the difficult solution conditions, Chu et al.[1-3] have used a unique high-temperature light scattering device for characterizing these polymers via dynamic and static techniques. Among other things, they have made determinations of the weight-average molecular weight ($\bar{M}_W$) and the molecular weight distribution (MWD).

An alternative technique for determining MWD has been developed using the storage modulus as a function of frequency, $G'(\omega)$, in the terminal relaxation zone for the polymer melt.[4] In brief, $G'(\omega)$ is a mirror of the cumulative MWD. Quantitative determinations are obtained by (1) transformation of the frequency axis to MW according to eq 1 and (2) transformation of the modulus axis to weight fraction through eq 2. In the above

$$1/\omega \propto (\mathrm{MW})^{3.4} \tag{1}$$

$$W_i = 1 - [G'(\omega_i)/G_N{}^{\circ}]^{0.5} \tag{2}$$

equations, ω is the measurement frequency in a dynamic rheological experiment, W_i is the weight fraction of the component whose MW corresponds to a specific frequency, ω_i, through eq 1, and $G_N{}^{\circ}$ is the plateau modulus. The method is calibrated by scaling a relative distribution to $\bar{M}_W$ using the well-known empirical relationship[5]

$$\eta_0 = K(\bar{M}_W)^{3.4} \tag{3}$$

where K is a proportionality constant. This latter step is done by measuring the zero shear viscosity, η_0, for the sample in question and determining $\bar{M}_W$ by an absolute method to obtain the constant K. This analysis assumes that we are analyzing a linear polymer in the melt state whose components have a MW greater than the critical value for entanglement. Derivation, validation, and utilization of the technique has been presented in detail elsewhere.[4,6-8]

This technique has been applied to other fluoropolymers, such as poly(tetrafluoroethylene)[6] and its copolymer with hexafluoroethylene)[6] and its copolymer with hexafluoropropylene.[7] Initial results have also been reported for PETFE where it was shown that distributions predicted by the rheological technique were broader than those predicted by dynamic light scattering.[8] It is the purpose of this report to offer an explanation for the discrepancy between the MWD predictions of the light scattering and rheological techniques.

Experimental Section

1. Polymers. Samples designated PETFE-1 through PETFE-3 are commercial samples of Tefzel manufactured by

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[*] Author to whom correspondence should be addressed.

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Table I
Summary of MWD Analysis for PETFE

	LLS data		rheological data	
sample	$\bar{M}_W \times 10^{-5}$	$\bar{M}_W/\bar{M}_N$	$\bar{M}_W \times 10^{-5}$	$\bar{M}_W/\bar{M}_N$
PETFE-1	5.4	1.4	5.3	2.9
PETFE-2	9.0	1.4	9.1	2.6
PETFE-3	12	1.4	12	2.7
PETFE-4	32	2.0	110	11
PETFE-1F (filtered)			4.9	2.7

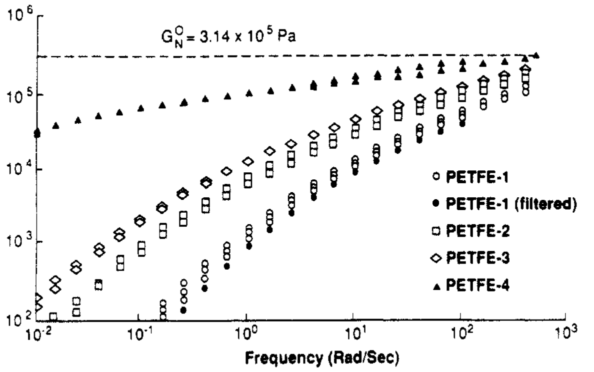

Figure 1. Storage modulus of PETFE samples as a function of frequency at 280 °C.

the Du Pont Co. The samples were polymerized with free radicals, and a chain-transfer agent was used to control the MW. They were characterized by laser light scattering (LLS) to determine their $\bar{M}_W$ and MWDs as described elsewhere.[1,2] The sample designated PETFE-4 was a specially prepared high-MW version of the same polymer whose molecular characterization was described previously, as well.[3] PETFE-4 was polymerized without a chain-transfer agent and thus represents the highest MW version of this sample which could be prepared in this manner. A summary of the LLS data for all samples is presented in Table I. Further details about these materials were also presented by Tuminello,[8] where PETFE-4 was referred to as UHMW-ETFE.

The sample designated PETFE-1F refers to a sample that was dissolved and filtered in a larger-scale version of the apparatus described by Chu et al.[1] About 1 g of this material was prepared and scrupulously dried prior to rheological analysis. It was prepared to simulate the material that was left in solution during the light scattering analyses.

2. **Rheological Measurements.** Dynamic measurements on all samples were made on a Rheometrics System IV rheometer at 280 °C using the parallel-plate geometry at 0.01–500 rad/s. Creep measurements were made at the same temperature for PETFE-4 on a Rheometrics constant-stress rheometer at the lowest possible shear rates, also using the parallel-plate geometry. Prior to measurement, the samples were compression molded into 2.54-cm-diameter disks of 0.1-cm thickness at 280 °C and about 2 MPa of pressure. The disks were loaded into the preheated rheometer, rapidly heated to 320 °C, and then rapidly cooled to 280 °C. This heating/cooling cycle was used to minimize the likelihood of any crystallinity being present during measurements. The widest temperature window experimentally available to us was about 270–320 °C. The storage modulus/frequency behavior was not very temperature sensitive over this range, making it unnecessary to carry out measurements at more than one temperature. In our experimental temperature window, the lower limit was the onset of recrystallization and the higher limit the onset of degradation. All measurements were made in a nitrogen atmosphere.

Results

1. **Modulus and Viscosity Data.** Plots of the storage modulus as a function of frequency, $G'(\omega)$, in the terminal zone for all samples are shown in Figure 1. At least duplicate runs were made for all samples except PETFE-1F (filtered). In the latter case, only enough sample was available for one set of measurements. In all cases, the samples which relax most rapidly [i.e., $G'(\omega)$ decreases most rapidly] have the highest concentration of chain-transfer agent and thus the lowest MW, as is expected.[5]

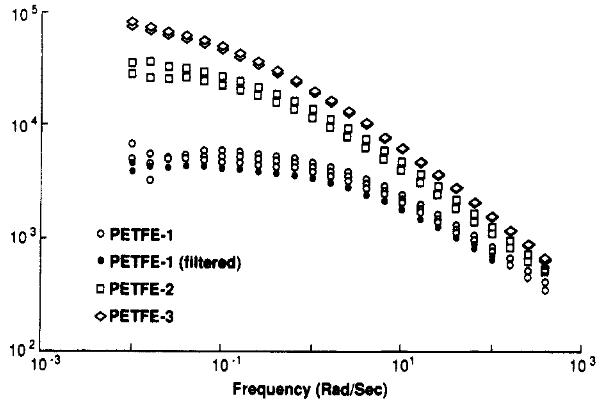

Figure 2. Dynamic viscosity versus frequency for the commercial PETFE samples at 280 °C.

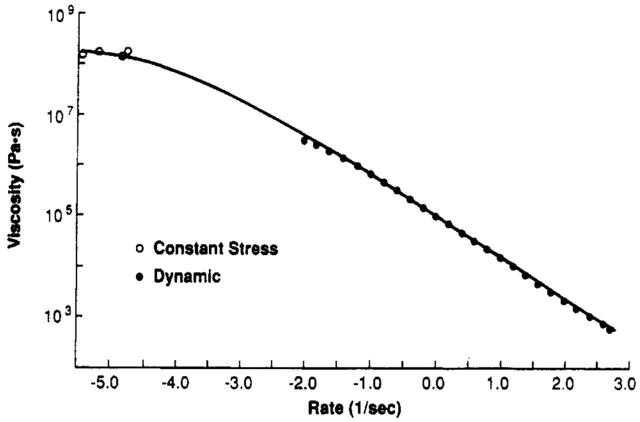

Figure 3. Dynamic viscosity versus frequency and steady-state viscosity versus shear rate for PETFE-4 at 280 °C.

The plateau modulus, $G_N°$, drawn in Figure 1 as 3.14 × 10^5 Pa was taken as the highest value measured for $G'(\omega)$. The classical method of determining $G_N°$ is integrating the $G''(\omega)$ curve in the terminal zone when a discernible peak is available.[5] However, there is no discernible peak in the $G''(\omega)$ plots for any of these samples, making this technique inapplicable. Choosing the highest value of $G'(\omega)$, as we did, at least gave us a lower limit to $G_N°$, since inspection of Figure 1 makes it obvious that $G_N°$ cannot be lower than this value.

The complex dynamic viscosity, $\eta^*(\omega)$, is plotted versus frequency for the commercial samples in Figure 2. It is again obvious that the samples made with the highest concentration of chain-transfer agent have the lowest values of the zero shear viscosity (η_0), where η_0 is the limiting viscosity at low deformation rate. Figure 3 is a plot of the viscosity versus rate curve for PETFE-4. In this case, the higher rate data are $\eta^*(\omega)$ measured dynamically and the lower rate data are the steady state viscosity as a function of shear rate from a creep experiment. Creep (constant stress) measurements had to be made because the frequencies available at our measurement temperatures were not low enough to determine η_0.

Values for η_0 are listed in Table II. They were determined by fitting eq 4 to the viscosity data in Figures 2 and 3. In eq 4, η is the rate-dependent viscosity and r

$$\eta = \frac{\eta_0}{[1 + Dr^{\delta}]} \qquad (4)$$

is the rate; D and δ are adjustable parameters. The rate,

Table II
Zero Shear Viscosities

sample	$\eta_0 \times 10^{-4}$ (Pa·s)	sample	$\eta_0 \times 10^{-4}$ (Pa·s)
PETFE-1	0.567	PETFE-4	15500
PETFE-2	3.59	PETFE-1F	0.439
PETFE-3	9.76		

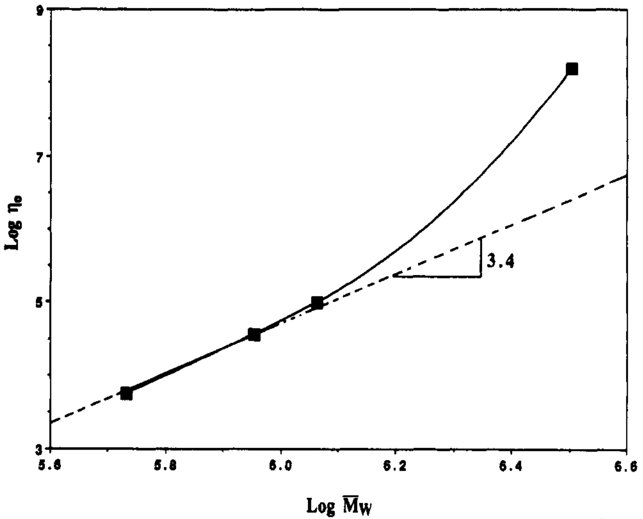

Figure 4. Zero shear viscosity versus weight-average MW for PETFE at 280 °C.

r, is either the oscillation frequency (ω) for the dynamic experiment or the shear rate, $\dot{\gamma}$, in a creep experiment. Obviously, η would then be either η^* or the steady-state viscosity, when r is ω or $\dot{\gamma}$, respectively.

2. MWD Determinations. MWDs were determined from $G'(\omega)$ according to the strict guidelines outlined for the tetrafluoroethylene/hexafluoropropylene copolymers.[7] We have described how we determined both G_N° and η_0 in the preceding section Modulus and Viscosity Data. These values are essential in solving eqs 1–3 for the MWD determinations. It is also necessary to determine the constant K in eq 3, in order to scale results to absolute values of the MW. According to eq 3, a double-logarithmic plot of η_0 from Table II versus $\bar{M}_W$ from the LLS data in Table I will have a slope of 3.4 with a y-intercept of log K. Such a plot is shown in Figure 4, and it is certainly not linear. An explanation for the nonlinearity is given in the Discussion section. The points representing the three lowest MW samples do fall on a straight line with an approximate slope of 3.4. The intercept of this line is −15.7, which is the value of log K.

A crucial part of the analysis is fitting the following equation to the modified version of the storage modulus, $[G'(\omega)/G_N^\circ]^{0.5}$, suggested by eq 2.

$$\left[\frac{G'(\omega)}{G_N^\circ}\right]^{0.5} = \sum_{i=1}^{n}\frac{1}{2}A_i\{1 + \tanh\,[B_i(X + C_i)]\} \qquad (5)$$

Equation 5 is thus an analytical representation of the data from which a continuous MWD can be deduced. In this equation, A_i, B_i, and C_i are the adjustable parameters; n is an integer which allows multiple terms to fit data representing complex distributions; X = log ω. The function represented by eq 5 is the identical shape of the cumulative MWD function; it is S-shaped with a minimum value of 0 at low ω and a maximum of 1 at high ω. The parameter A_i controls the height, or maximum value of each term. Additionally, $\sum A_i = 1$ with $0 < A_i < 1$. B_i controls the curve width, and C_i locates the curve on the X axis. The optimum value for the integer n was 2 for all samples except PETFE-1 and -1F, where it was 1. Table III gives the parameters we chose from this curve-fitting operation. Plots of $[G'(\omega)/G_N^\circ]^{0.5}$ with fitted curves from eq 5 are shown in Figure 5. The criteria for choosing the optimum number of terms in eq 5 (i.e., the value of n) were outlined in a previous publication.[7] If n = 1, only symmetrical distributions can be represented on semilog plots. Both visual and statistical criteria were used for deciding whether more than one term of eq 5 is necessary in the fitting process.

Table III
Parameters for FORTRAN Curve Fits of Equation 5

sample	A_1	B_1/B_2	C_1/C_2
PETFE-1	1.000	0.579/-----	−2.237/-----
PETFE-2	0.452	0.655/0.953	−0.579/−2.446
PETFE-3	0.653	0.574/1.379	−0.699/−2.293
PETFE-4	0.666	0.424/0.982	1.809/−1.492

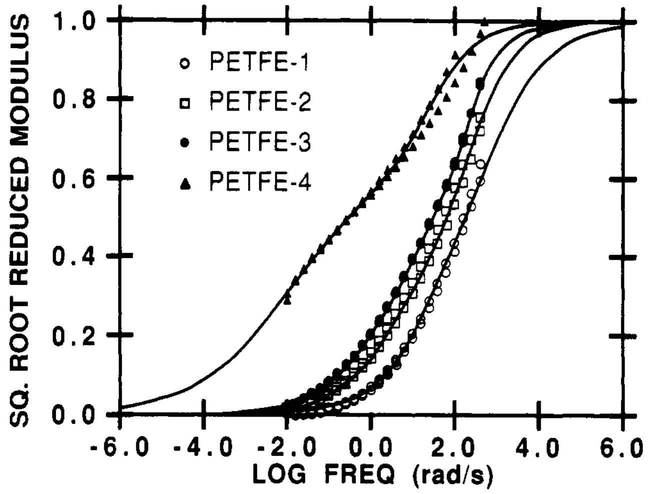

Figure 5. Transformed modulus–frequency plots, $[G'(\omega)/G_N^\circ]^{0.5}$. The model fits using eq 5 are represented by the solid lines drawn through the data points. The adjustable parameters used in these fits (A_i, B_i, C_i) are listed in Table III.

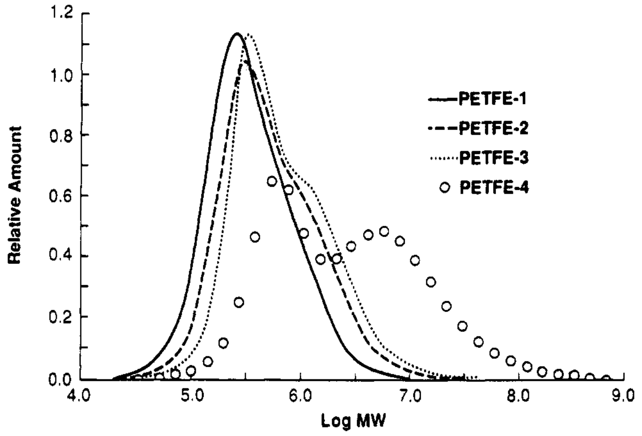

Figure 6. Differential MWD plots for PETFE.

The remaining steps to determining the MWD were identical to those described previously.[7] The differential MWDs are shown in Figure 6. The MWD averages and polydispersity ratios, $\bar{M}_W/\bar{M}_N$, are listed next to the LLS data in Table I.

Discussion

The MWD results from the light scattering and rheological experiments can be compared in Table I. There are two obvious discrepancies. First, the light scattering always gives narrower distributions. Second, using the constant K determined from the three lowest MW samples,

Table IV
Effect of Plateau Modulus on the Polydispersity Ratio for PETFE-2

$G_N{}^0 \times 10^{-5}$ (Pa)	$\bar{M}_W/\bar{M}_N$	$G_N{}^0 \times 10^{-5}$ (Pa)	$\bar{M}_W/\bar{M}_N$
5.77	4.4	1.00	1.9
3.14	2.6	0.50	1.7
2.35	2.4		

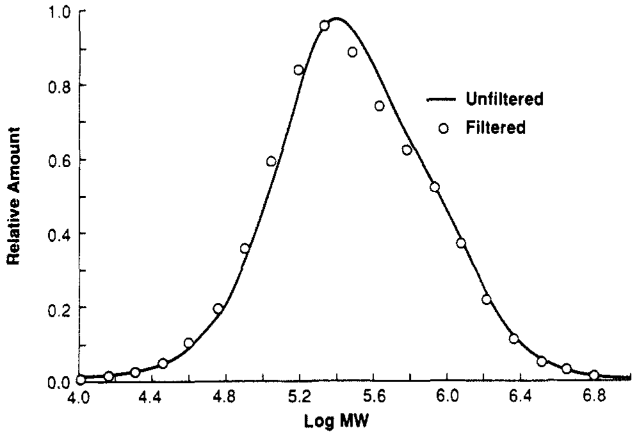

Figure 7. Comparison of differential MWD plots for filtered and unfiltered PETFE-1.

the $\bar{M}_W$ determined for PETFE-4 from rheology was much larger than that determined from light scattering.

We have thought of three possible reasons for the discrepancies. (1) The value we chose for $G_N{}^\circ$ is too high. (2) A high MW or gel fraction was filtered out of the sample during preparations for the LLS experiment. (3) There is long-chain branching present in the polymer. The remainder of this paper will investigate the validity of each of these explanations.

1. **Plateau Modulus.** We determined the effect of varying the value of $G_N{}^\circ$ on the polydispersity ratio for sample PETFE-2. The results are shown in Table IV. As was mentioned in a previous section, the value we chose for $G_N{}^\circ$ (3.14×10^5 Pa) was considered to be the lower limit for PETFE. Therefore, any value lower than 3.14×10^5 Pa is unlikely. According to Table IV, it requires a ridiculously low value ($<5 \times 10^4$ Pa) to obtain the polydispersities predicted from LLS. Also, changing the value of the plateau modulus would not affect the differing values obtained for the $\bar{M}_W$ of PETFE-4. Therefore, we discount the plateau modulus as being the cause of the discrepancies between the LLS and rheological results.

2. **Filtered Component.** One obvious explanation for the discrepancies is that an insoluble polymer fraction (very high MW or cross-linked) was filtered from the dilute solution prior to light scattering measurements. If this were true, LLS results would indicate a lower MW and narrower distribution than a technique, such as melt rheology, which analyzed the entire sample. To test this hypothesis, we prepared a sample of the filtered material, PETFE-1F, as described in the Experimental Section, for melt rheological analysis. Table I shows that the polydispersity ratio for the filtered sample is not significantly different from that of the unfiltered sample, PETFE-1. Also, comparing the differential distribution plots in Figure 7 reveals no significant differences. Therefore, filtering of insoluble high MW or gel components can be ruled out as the cause of the discrepancies between LLS and rheological results.

3. **Long-Chain Branching.** Long-chain branching could be considered the cause of the discrepancies by default, but there are more compelling reasons for the choice. Carella et al.[9] have shown that nearly monodisperse "star" polymers, with equal length arms, have much broader relaxation time distributions than their linear counterparts. This means that $G'(\omega)$ decreases much more gradually from $G_N{}^\circ$ for the branched polymers than for linear ones with identical MWDs. Another way of saying this is that the presence of long-chain branching has the same effect on $G'(\omega)$ as broadening the MWD. Since $G'(\omega)$ is a mirror of the MWD,[4] using the MWD determination described in this paper would make a branched polymer appear much more polydisperse than it is. The light scattering, being mass sensitive, would not be affected by the presence of branching. The polydispersity discrepancies are thus adequately explained by the presence of long-chain branching.

Current knowledge prevents us from further modifying the MWD determination for a branched polymer. Equations 1 and 3 most certainly would have to be modified. It is also possible that eq 2 would need modification. Equations 1 and 3 deal with the power laws relating measurement frequency and zero shear viscosity, respectively, to MW. It has been shown[9] that η_0 and probably ω as well are functions of both the number of branches and the length of these branches. Since neither of these things are known about PETFE currently, it would be a fanciful exercise to modify the MWD results.

The unusual shape of the viscosity–MW plot in Figure 4 is also consistent with the presence of branching. In a summary of several publications of his and his co-workers' efforts, Graessley[10] has shown that long-chain-branched polymers show similar behavior. At lower MWs the 3.4 power law (eq 3) seems to be obeyed. At higher MWs, however, the viscosity increases in a much stronger manner with MW.

A potential mechanism for forming the branches could involve portions of the polymer molecule acting as its own chain-transfer agent. PETFE has unusual chemical inertness for a polymer with 50 mol % ethylene. It is felt that the predominantly alternating nature of the copolymerization is the cause of this, with adjacent CF_2 groups "shielding" the smaller CH_2 groups. The structure is not perfectly alternating, however. Significant numbers (10%) of tetrafluoroethylene diads have been found using ^{19}F NMR.[11] Calculations based on reactivity ratios predict that about 5–10% ethylene will exist as diads. These ethylene diads will have the middle two methylene groups essentially unshielded from chemical attack. The hydrogens on these unshielded methylenes may thus be expected to be subject to abstraction by a free radical during polymerization. The branches could be produced when the radical end on one growing chain abstracts a hydrogen from one of the unshielded methylene groups on a second polymer chain. This would leave an active radical in the middle of the second chain. Further polymerization from this site would yield a side chain which could grow to the same length as the average unbranched molecule.

One could also argue that the light scattering results for $\bar{M}_W/\bar{M}_N$ appear too narrow for a chain-transfer terminated free-radical polymerization; theory[12] predicts $\bar{M}_W/\bar{M}_N$ should be no greater than 2. Broader distributions would result with chain transfer to the polymer chain, which we have proposed for PETFE. Therefore, the light scattering results of $\bar{M}_W/\bar{M}_N \sim 1.5$ appear not to be correct. However, the theory used in these predictions assumes homogeneous polymerization, and the polymers analyzed in this study were synthesized in a heterogeneous environment. The authors therefore feel uncomfortable impuning the light scattering results based on such theory.

Conclusions

We have shown that rheology predicts broader MWDs for PETFE than LLS. We also showed that the viscosity–MW plot has an unusual shape. Neither the uncertainty in the plateau modulus value nor filtered insolubles could explain these observations. Long-chain branching was shown to be a plausible explanation. Ethylene diads could conceivably act as chain transfer sites to promote this branching.

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